Solar Photocatalytic Degradation of Environmental Pollutants Using ZnO Prepared by Sol-Gel: 2, 4-Dichlorophenol as Case Study

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Abstract

The photocatalytic degradation of 2, 4-dichlorophenol (2,4DCP) in aqueous solution was carried out in batch process with ZnO prepared by sol-gel method. The effects of various factors, such as different calcinations temperatures and amount of catalyst were investigated for efficient degradation of 2, 4-dichlorophenol. The UV/Vis Spectrophotometer was used for analyzing the concentration of 2, 4-dichlorophenol in solution at different time intervals during the experiment. The photocatalytic degradation of 2, 4-dichlorophenol was investigated by monitoring molecular absorbance at $\lambda = 285$ nm. The average solar intensity of ultra violet (UV) was recorded as 23 W/m^2. The photocatalyltic activity of the ZnO was evaluated by photocatalytic degradation of initial concentration 50 mg/l of 2, 4-dichlorophenol. Optimum value of catalyst dose was found to be 2 g/l. The experimental results showed that the photocatalytic degradation efficiency of 2, 4-dichlorophenol for 1 h irradiation time was up to 98 %.

Keywords: Solar photocatalytic; Sol-gel; 2, 4-dichlorophenol

1. Introduction

Phenols and their chlorinated derivatives represent one of the most abundant families of industrial toxic compounds which are resistant to biodegradation and persist in the environment for long periods [1,2]. These pollutants originate from a large number of different sources, the most important among them being the effluents of the petroleum and petrochemical industries, Kraft Mills, Olive Oil production, and various chemical manufacturing industries such as those producing phenolic resins, herbicides, pesticides, solvents, paints, plastics and other chemicals [2-5]. Chlorophenols are well-known environmental pollutants owing to their high potential of phytotoxicity and zootoxicity. In particular, 2,4-dichlorophenol (DCP) has been listed by US EPA as a priority pollutant which the community has right to know [6,7]. 2,4-Dichlorophenol (2,4-DCP) is a precursor to the manufacture of the widely used herbicide 2,4-dichlorophenoxy acetic acid (2,4-D) and is also the major transformation product of 2,4D caused by solar photolysis and also microbial activities in soil or natural water. The toxic and bio-resistant organochlorine compounds in aqueous systems need to be transformed into harmless species.

Biological oxidation requires longer retention time and thus not suitable for high concentrations of pollutants or for persistent pollutants. Increasing amount of work has therefore been devoted to finding an efficient, inexpensive, and green chemical degradation process for these persistent organic chemicals, thus making catalytic oxidation a highly favored process [8]. Heterogeneous photocatalytic oxidation has received overwhelming interest as a potential efficient method in the degradation of recalcitrant environmental contaminants [9, 10].

Among the various advance oxidation processes (AOPs), semiconductor mediated photocatalysis has over the last few years , proved to be of greater advantage due to its ability to destroy a wide range of organic and inorganic pollutants at ambient temperature and pressure, without the generation of harmful by- products. The ZnO appears to be an economical alternative since it has been reported that it also induces photocatalytic degradation of organic compounds [11]. When a ZnO photocatalyst is irradiated with UV light electrons move from the valence band to the conduction band (e$^-$), leaving positive holes (h$^+$) behind [12]. These highly reactive species (e$^-$ and h+) initiate oxidation and reduction reactions on the surface of ZnO particles. In an aqueous suspension, h$^+$ reacts with surface OH$^-$ groups to give HO$^\bullet$ radicals, which are

known to be strong oxidizing species. In addition to this, (e^-) reacts with adsorbed molecular O_2 to produce an $^\cdot O_2^-$ superoxide anion radical that can also contribute to the production of $HO^\cdot$ radicals and H^+. It is believed that the reaction of $HO^\cdot$ radicals with organic pollutants eventually leads to mineralization of these compounds [13]. The photocatalytic degradation process can be summarized by the following reactions:

$$ZnO + h\upsilon \rightarrow e^- + h^+ \tag{1}$$

$$H_2O + h^+ \rightarrow {}^\cdot OH + H^+ \tag{2}$$

$$O_2 + e^- \rightarrow {}^\cdot O_2^- \tag{3}$$

$$^\cdot O_2^- + H^+ \rightarrow {}^\cdot HO_2 \tag{4}$$

$$^\cdot O_2^- + H^+ + {}^\cdot HO_2 \rightarrow O_2 + H_2O_2 \tag{5}$$

$$H_2O_2 + H^+ + (e^-) \rightarrow {}^\cdot OH + H_2O \tag{6}$$

$$\text{Polychorophenol} + {}^\cdot OH \rightarrow CO_2 + H_2O + H^+ + Cl^- \tag{7}$$
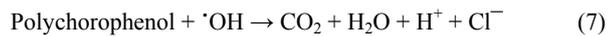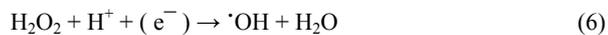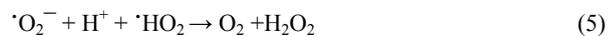
The sol–gel process is one of the versatile methods used to prepare high pure and nano-size materials shaped as powders or coatings [14]. This method has many advantages over other production techniques, including ease of processing, control over the composition, purity and homogeneity of the obtained materials [15]. This approach does not need complicated instruments such as chemical vapor deposition. It provides a simple and easy method to synthesize nano-size photocatalysts. In the present work a ZnO nano-catalysts was synthesized, characterized and used in the photocatalytic degradation of 2, 4-dichlorophenol under sunlight irradiation.

2. Experimental and methods

2.1. Materials

2, 4-dichlorophenol (assay 99%, λ_{max}= 285 nm) was obtained from sigma Aldrich. Zinc acetate $(C_4H_{10}O_6Zn)$ and ethanol absolute (C_2H_6O) were obtained from Merck Chemical Company (Darmstadt, Germany), and oxalic acid $(H_2C_2O_4)$ from R&M chemicals Malaysia. De-ionized water was used for preparing all standard solutions. All chemicals were used without further purification.

2.2. Preparation of ZnO photocatalyst

ZnO catalyst was prepared by sol–gel method from zinc acetate in a solution of oxalic acid, using ethanol. Zinc acetate (3.66 g) was dissolved in 100ml ethanol and refluxed at 75 °C under vigorous stirring for 30 min. Oxalic acid (4.2 g) was mixed with 75 ml of ethanol and added to the previous solution drop wise. The final mixture was refluxed at the 50 °C for 60 min and then left to cool down to room temperature. Finally the gel was dried at 80°C overnight (Xerogel) and the powder calcined for 3 h at different temperatures, 400,500 and 600°C.

2.3. Characterization

The crystallinity of ZnO powder samples were analyzed by X-ray power diffraction using D8 Advance Brukur AXS X-ray diffractometer with CuKα radiation (λ=1.54062 Å) in the 2θ scan range of 20-80°. The UV-Visible spectrum of ZnO catalyst (Reflectance %R) was recorded in the range 200-600 nm using Perkin Elmer (lambda 35) UV/Vis Spectrophotometer. The specific surface area (BET) was determined by Nitrogen gas adsorption-desorption isotherms using Alt amira Instruments, Model AMI 200.

2.4. photocatalytic reactor and Analysis

The photodegradation of 2,4-dichlorophenol was carried out using the non-concentrating type slurry reactor of dimension 3.5 cm high and 6.5 cm diameter. The average UV intensity of sunlight was recorded 23 W/m^2 during the experiments. The intensity of UV sunlight was measured by Skyelynx type SDL 5100. The COD tests were carried out according to close reflux, colorimetric method using Hach DR/2010 Spectrophotometer and Hach COD reactor [16]. The estimation of chloride ion concentrations as function of irradiation time was carried out using a Metrohm (882 compact IC plus) Ion Chromatograph.

2.5. Degradation experiments procedures

The degradation experiments were performed in the presence of the ZnO catalyst at different amount (1, 2, 3 g/l) added to 100 ml of 50 mg/l concentration of 2,4-dichlorophenol for each run. The aqueous suspension was magnetically stirred for 1 hr under dark for equilibrium. The suspension was subjected to irradiation under solar light. Aliquot was taken out at different time intervals with the help of a syringe and then filtered through a 0.2 μm filter. The rate of degradation was studied in terms of change in absorption spectra at λ_{max} = 285 nm, which is representative of describing the disappearance of 2,4-dichlorophenol and redaction in chemical oxygen demand (COD). The percentage degradation was calculated as follows:

$$\% \text{ Degradation} = \left(\frac{C_o - C}{C}\right) \times 100 \tag{8}$$

where C_o is the equilibrium concentration of 2,4-DCP and C, is concentration of 2,4-DCP at solar irradiation time.

3. Results and discussion

3.1. Characterization of ZnO photocatalyst

Fig.1 shows the powder X-ray diffraction patterns of ZnO prepared by sol-gel method. The gel was dried at 80 °C (Xerogel) without calcination shows a poor crystallinity. Fig. 1(a,b,c) shows XRD patterns of ZnO annealed at, 400, 500 and 600°C for 3 hr. All peaks were observed in accordance with zincite phase of ZnO (International Center for Diffraction Data, JCPDS) [17].
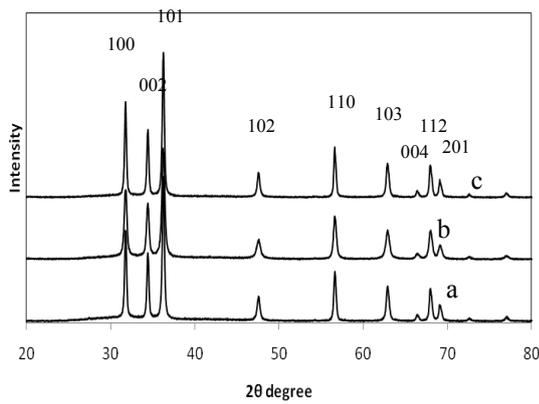
Fig.1. XRD pattern of the ZnO powder product obtained at various calcining temperature (a) 400 ºC (b) 500 ºC (c) 600 ºC

No peaks for impurity were observed, suggesting that a high purity ZnO was obtained. As is shown in Fig 1, it can be seen that the higher the heat treatment temperature is the crystal phase of sample becomes more perfect and some crystal grains agglutinate and become bigger. In addition, the peak is widened implying that the particle size is very small according to the Debye-Scherer formula [18].

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (9)$$

K is the Scherer constant, λ the X-ray wavelength, β, the peak width of half maximum, and θ is the Bragg diffraction angle. The crystallite sizes D are calculated from main peak (101) of ZnO using the Debye-Scherer formula and shown in Table 1.

Table 1. Summary of the properties and heat treatment conditions of samples

Temperature (ºC)	400	500	600
Surface area(m^2/g)	48.37	25.46	21.84
Crystal size(nm)	14.9	26.8	28.9

From Table 1, it is can be seen that the surface area of ZnO photocatalyst decreases as the crystal size increases. This indicates that a decrease in surface area is mainly due to growth of crystal size. The best heat treatment preparation condition (calcination) is at 400 ºC for 3 hr. The similar results were reported by [19].

The optical reflectance spectra of ZnO catalyst sample thermally decomposed at 400ºC for 3 h is shown in Fig.2. The UV-Visible absorption spectrum of the sample exhibits strong absorption spectra of all below 400 nm. The direct band gap (E_g) of the sample is determined by fitting the absorption data to the direct transition equation:

$$\alpha h\nu = E_d (h\nu - E_g)^{1/2} \qquad (10)$$

where α is the optical absorption coefficient, hν is the photon energy, E_g is the direct band gap, and E_d is a constant [20].

Plotting $(\alpha h\nu)^2$ as a function of photon energy, and extrapolating the linear portion of the curve to absorption equals to zero as shown in Fig. 2(b) and this gives the value of direct band gap (E_g) as 3.11eV. The band gap (E_g) value of ZnO catalyst sample at 400ºC is close to the band gap value of ZnO reported by [21].
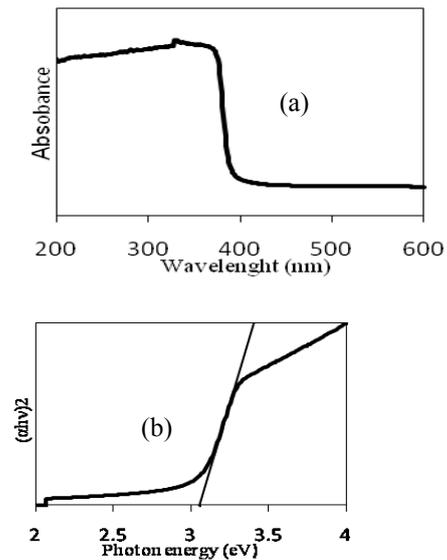
Fig.2. (a) Optical absorption spectrum of ZnO catalyst annealed at 400 ºC (b) Energy band gap (Eg)

3.2. Photocataytic activity

3.2.1. UV-vis spectra

The degradation of 2,4-dichlorophenol with solar time exposure was recorded. Fig.3 shows absorption peak was observed at 285 nm. This decreases gradually indicating that the decomposition of the organic compound was taking place.
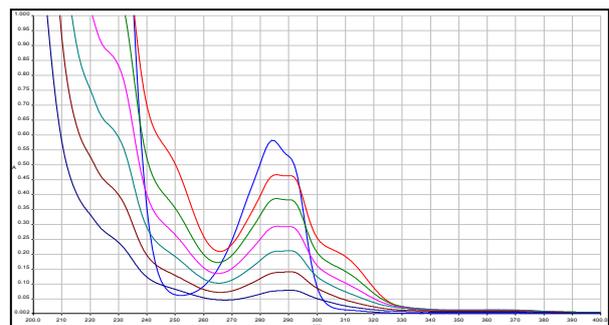
Fig.3. Time dependent absorption spectra of 2,4-DCP under solar radiation

3.2.2 Photocatalytic degradation of 2,4 DCP by ZnO

Photodegradation of 2,4-dichlorophenol (50 mg/l initial concentration) solution having a pH value of 5.5 was studied by exposing the solution to solar irradiation in absence and presence of 1, 2 and 3 g/l ZnO as photocatalyst. The irradiation in absence of the ZnO showed only 5% destruction in 1hr, whereas in the presence 1g/l of the ZnO, 67% 2,4-dichlorophenol was degraded during same time. The weak degradation of 2,4-dichlorophenol in the absence of ZnO is assigned to the direct photolysis resulting in weak UV light absorption by the 2,4-dichlorophenol. A comparison of these results, showed that the direct photolysis has negligible effect as compared to heterogeneous photocatalytic process on the degradation of 2,4-dichlorophenol.
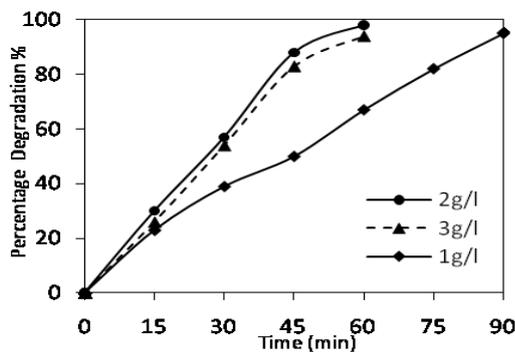
Fig.4. Effect of different of ZnO catalyst loading on degradation of 2,4-DCP under solar radiation (50 mgl-1 ,pH=5.5)

When degradation studies of 2,4-dichlorophenol were carried out with 2 g/l of ZnO , it was found that percentage degradation 98% occurred within almost 1hr. This may be due to the fact that as the quantity of ZnO increased, the number of 2,4-dichlorophenol molecules adsorbed was also increasing owing to an increase in the number of ZnO particles. As the amount of photocatalyst increases, the percentage degradation increases and it starts decreasing slowly by using 3 g/l as shown in Fig. 4. Further increase in the amount of ZnO catalysts showed a negative effect of photodegradation, due to an increase in turbidity of the suspension with high loading of photocatalyst, there was a decrease in the penetration of UV light and hence photoactivated volume of suspension decreases [22, 23].

3.2.3. Chemical oxygen demand (COD) removal

As the reduction in chemical oxygen demand (COD) reflects the extent of degradation of an organic species. The COD removal of 50 mg/l of 2,4-dichlorophenol was studied under different loading of ZnO as function of irradiation time. Fig.5 shows that results of COD removal were increased with degradation of the 2,4-dichlorophenol increases [24,25]. About 96% COD reduction was achieved with 2 g/l within 1hr compared with 1 g/l only 89% COD reduction which was noticed during 1.5 hr radiation time.
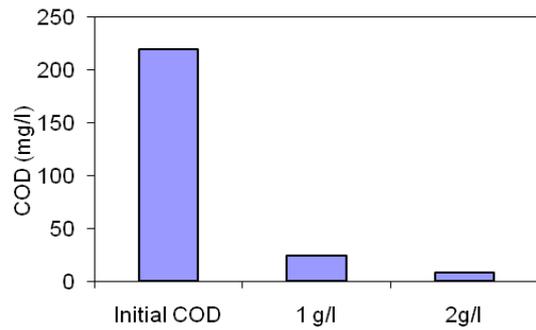
Fig.5. Effect of ZnO photoctalyst amount on COD removal of 2, 4-DCP under solar radiation

3.2.3. Dechlorination of 2, 4-dichlorophenol by ZnO

In photocatalytic degradation of 2,4-dichlorophenol using ZnO, the produced hydroxyl radical will attack the aromatic ring of 2,4-dichlorophenol. Fig.6 shows the concentration of free ion chloride Cl^- produced during the oxidation of 2,4-dichlorophenol at different loading of ZnO catalyst. As shown in Fig.6, the Cl^- generated had their maximum values by using 2 g/l amount loading of ZnO catalyst, due to activity of degradation higher than 1 g/l and completed destruction of 2,4-dichlorophenol.

3.2.4. Reusability of ZnO photocatalyst

Reusability of ZnO for the degradation of 2,4-dichlorophenol by photocatalysis process was evaluated. The ZnO was filtered after photcatalytic degradation, washed several times by water and ethanol and dried. The dried ZnO catalyst samples were used for the degradation of 2,4-dichlorophenol ,at similar experimental conditions. The efficiency of degradation was found almost same as the initial efficiency after two times cycles. ZnO catalyst showed a considerably reproducible photocatalytic activity up to two cycles for degradation of 2,4-dichlorophenol.
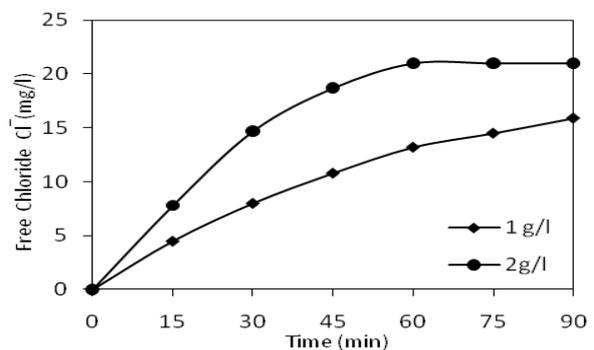
Fig.6. Free chloride concentration during the photocatalytic degradation of 2, 4-DCP under solar radiation

3. Conclusion

Zinc oxide photocatalyst was prepared by the sol-gel method using Zinc acetate as the raw material. ZnO has been found to be a better photocatalyst for the degradation of 2,4-dichlorophenol.

Optimum calcination was observed to be about 400^oC. Experimental results indicated that the initial rate of photodegradation increased with increase in catalyst amount showed up to an optimum loading (2 g/l).

Further increase in catalyst loading showed a negative effect.

This study may provide a versatile approach as a highly efficient method for the degradation of toxic compounds of poly chlorinated phenol (PCPS) under sunlight.

Nomenclature

C_o	Equilibrium concentration of 2,4-DCP, mg/l
C	concentration of 2,4-DCP at solar irradiation time mg/l
D	average crystallite size, nm
K	The Scherer constant
E_d	Constant
E_g	The direct band gap, eV
Λ	X-ray wavelength, nm
B	Peak width of half maximum
Θ	Bragg diffraction angle, degree ^{o}
A	Optical absorption coefficient
$H\nu$	Photon energy, eV

Acknowledgments

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